

## WOOD COFIRING EXPERIENCE IN CYCLONE BOILERS

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Key Words: wood waste, cyclone boilers, cofiring

### ABSTRACT

Wood waste has been cofired with coal in cyclone boilers at the Allen Fossil Plant of TVA, the King Station of Northern States Power Co., and other generating stations. This practice is sufficiently interesting that TVA plans long term testing of cofiring wood at Allen. This practice can be separate from, or combined with, cofiring tire-derived fuel (TDF) in cyclone boilers. Cofiring has been practiced with the wood waste being fed to the boilers simultaneously with the coal, and with the wood waste being introduced into the secondary air system of cyclone boilers, for separate feeding. The practice of cofiring wood waste with coal in cyclone boilers has been shown to reduce emissions of  $\text{SO}_2$  and  $\text{NO}_x$ , while also reducing the cost of fuel in selected locations. Foster Wheeler Environmental Corporation has evaluated this practice both with engineering design studies and with field testing for the Electric Power Research Institute and the Tennessee Valley Authority. This paper summarizes testing and experience in several locations, focusing upon the following issues: 1) the impact of cofiring on boiler performance and consequent airborne emissions, 2) the alternative designs to accomplish cofiring, and 3) the economics of cofiring under various conditions.

### INTRODUCTION

Cofiring of biofuels with coal provides utilities with the opportunity to accomplish the following objectives: 1) reduce fuel costs by utilizing residuals from the forest products industry; 2) reduce formation of  $\text{SO}_2$  by using a fuel which contains virtually no sulfur; 3) reduce formation of  $\text{NO}_x$  by using the biofuels that are low in nitrogen and that burn at lower temperatures than most coals (e.g. wood wastes; some agricultural materials can be high in nitrogen and therefore do not satisfy this objective); 4) reduce the formation of  $\text{CO}_2$  from fossil fuels, thereby addressing issues associated with the global climate challenge; and 5) support economic development in the utility's service area, thereby enhancing baseload customer growth and plant utilization. All of these objectives are mandated by law and regulation, results of voluntary utility actions (e.g. fossil  $\text{CO}_2$  reductions), or are conventional utility practice for managing costs and loads.

From a materials handling and fuel preparation perspective, the biofuels are fundamentally different from coal. They can not be ground by traditional pulverizing methods, but must be shredded or chopped. Biofuels are fibrous. Consequently, fuel preparation methods can be fundamentally different. Biofuels respond to hammermills and derivative systems, but not to ball mills, bowl mills, and other coal pulverizing technologies. The additional material handling property of consequence is bulk density. Coal is typically on the order of 40 - 50  $\text{lb/ft}^3$  while wet wood is on the order of 18 - 20  $\text{lb/ft}^3$ , dry wood is about 10 - 12  $\text{lb/ft}^3$  and most agricultural wastes are on the order of 8 - 12  $\text{lb/ft}^3$  as well. These bulk densities require careful management practices such that the fuel storage system is not compromised when cofiring is considered.

Chemically, biofuels, particularly wood waste, are fundamentally different from coal as is shown in Table 1. As mentioned previously, biofuels are low in sulfur content. Further the wood wastes are typically very low in nitrogen content, although some agricultural wastes including rice hulls and alfalfa stems may have nitrogen contents that are at moderate to high levels (e.g. 0.5 - 2.0%, dry basis). These fuels are somewhat oxygenated, typically moist, and have modest heat contents. Of more consequence, these fuels can have low to moderate ash percentages (e.g. 3 - 6%). The ash, however, is fundamentally different from coal with high concentrations of alkali metals: potassium, calcium, and sodium.

Base/acid ratios are in the range of 2.0 - 6.0, with some B/A values exceeding 10.

The behavior of biofuel/coal blends in combustion systems can be readily predicted from weighted arithmetic averaging of the properties of the individual fuels, with particular attention to proximate and ultimate analysis, higher heating value, and formation of combustion products. The one exception is ash fusion temperature, where blending shifts the base/acid ratio towards 1.0, and consequently impacts ash fusion temperatures according to the following equations:

$$AFT_i = 1268.7W^2 - 980W + 2336 \quad [1]$$

$$AFT_h = 1025.9W^2 - 494W + 2069 \quad [2]$$

Where  $AFT_i$  is the initial deformation temperature,  $W$  is the weight percentage of wood (dry basis) in the blend, and  $AFT_h$  is the hemispherical temperature (reducing environment).

The high concentration of alkali metals in the ash further complicates the analysis based upon the potential for slagging and fouling. The potassium oxide is of particular concern due to the low temperatures at which it vaporizes, leading to the potential for condensation in backpasses of the boiler.

The consequence of these characteristics is that biofuel cofiring, particularly wood cofiring, is more readily achieved with cyclone boilers than with pulverized coal (PC) boilers; this ease of accomplishment is particularly apparent at moderate cofiring percentages which are on the order of 10 - 15% by heat input or 20 - 30% by mass.

#### BACKGROUND

Within the past few years, several utilities have initiated cofiring experiments or practices. Northern States Power (NSP) has initiated cofiring at its cyclone-based King Station, and consumes wood waste from the Andersen Windows manufacturing plant on a regular basis. This practice has gone on for the past several years, and NSP has been very successful. Cofiring occurs in 3 of the 12 cyclone barrels at the plant, and firing levels of 15% wood (heat input basis) have been achieved. The wood, which is dry and pulverized, is introduced through the secondary air system. Wood fuel storage and preparation is separated from coal storage and preparation. The Big Stone Plant of Otter Tail Power also has cofired wood waste in the form of railroad ties. This plant, also a cyclone boiler, was designed for lignite. It has provisions for fuel drying. It also has a very large primary furnace in order to ensure burnout of char particles.

TVA and EPRI initiated cofiring investigations in 1992. The investigations included both PC boilers and cyclone boilers, with the latter focusing upon cofiring at the Allen Fossil Plant (ALF) in Memphis, TN. The concept developed had broader application than the design used at the King Station of NSP: in this concept, wood waste is mixed with coal in the fuel yard and simultaneously transported to the fuel bunkers and then to the cyclone burners. TVA also contemplated using green wood (40 - 50% moisture) as opposed to the dry wood (8 - 12% moisture) being fired at the King Station of NSP (See Fig 1).

#### EPRI/TVA INVESTIGATIONS

The EPRI/TVA investigations, through Foster Wheeler Environmental Corporation (then Ebasco Environmental Corporation) were initiated by development of conceptual process designs and associated calculations. These were followed by mechanical systems designs, cost estimates, evaluations of environmental impacts, and economic assessments.

The studies generally demonstrated that cofiring at 10% by heat input, or 20% by mass, would have the following impacts: 1) not affect the ability of the plant to achieve capacity based upon fan capacities and related factors, 2) reduce boiler efficiency by about 1.5%, depending upon the specific condition of the wood, 3) reduce the  $SO_2$  emissions as a function of fuel substitution, and 4) reduce  $NO_x$  emissions disproportionately based upon fuel effects

(reduced nitrogen content in the fuel) and temperature effects in the cyclone barrel.

The initial designs, calculations, and evaluations led to the conclusion that cofiring would be economically feasible at the ALF location. The economics were favorable as a consequence of the following factors: 1) a low capital cost (\$130 - \$200/kW supported by wood waste), a fuel price differential of \$0.40/10<sup>6</sup> Btu between wood and Western Kentucky bituminous coal delivered to the site, 3) modest incremental operating and maintenance costs utilizing one additional person and capitalizing upon existing maintenance infrastructure at the plant, and 4) modest credits for SO<sub>2</sub> removal (\$136/ton SO<sub>2</sub> based upon recent market prices). No credits were taken for NO<sub>x</sub> or fossil CO, although they are the source of significant economic analysis.

The initial investigations led to a week of parametric testing at the facility. The testing involved evaluations of the ability to achieve capacity at ALF when cofiring wood with coal, boiler efficiency when firing wood and coal at various levels, and reductions in airborne emissions. The testing program involved cofiring at percentages ranging from 1.6 to 20%, mass basis. The wood was obtained from local sources, and the coal was a Western Kentucky coal (see Table 1).

The testing confirmed the results from the calculations: capacities were largely not impacted by cofiring, boiler efficiencies were reduced by less than 2% when cofiring even at significant wood percentages, SO<sub>2</sub> emissions declined in proportion to the Btu substitution of wood for coal, and NO<sub>x</sub> emissions declined in response to fuel substitution and temperature effects.

Additional testing performed under this program involved storage and flow characteristics of wood/coal blends; and this work was performed largely by Reaction Engineering International in support of the Foster Wheeler Environmental program. This testing demonstrated that wood waste improved the flow of fuel through the bunkers, and virtually eliminated dusting on the coal belts. Additional testing performed by Foster Wheeler Environmental also documented that the wood did not compromise storage from the perspective of inducing spontaneous combustion.

The parametric tests and supporting investigations were initial indications of the potential for wood cofiring. They have resulted in the decision to pursue additional tests during the first half of 1995, pursuant to commercializing cofiring using the system shown in Fig. 1. These tests will be conducted firing wood with Utah bituminous coal, and with combinations of coal, wood, and tire-derived fuel (TDF).

#### CONCLUSIONS

The cofiring program conducted at the Allen Fossil Plant of TVA is advancing to extended testing, more detailed materials handling engineering, and additional economic analyses. This program integrates the EPRI/TVA approach to cofiring into the range of options being pursued by other utilities. Such utilities are testing cofiring wood waste at low percentages in PC boilers, transporting <5% wood (mass basis) through the pulverizers with the coal. Such testing is also considering cofiring wood in PC boilers at higher percentages, using separate biofuel preparation. These systems fire the biofuels through dedicated burners into the boiler. Utilities pursuing such options include TVA as well as Georgia Power, Savannah Electric, New York State Electric and Gas, and others. The cofiring program at the Allen Facility has not yet completely proven the commercial viability of cofiring in cyclone boilers using the design configuration shown in Fig. 1; however the program is sufficiently advanced that such commercial demonstration is anticipated as a consequence of the next sequence of tests plus some planned long term test activities.

#### ACKNOWLEDGEMENTS

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Table 1. Typical Fuel Compositions for Eastern Bituminous Coal, Wood, and Alfalfa Stems

	Bituminous Coal	Wood Fuel	Alfalfa Stems
Proximate Analysis (wt %, dry basis)			
Volatile Matter	37.22	84.58	76.03
Fixed Carbon	52.97	14.26	17.45
Ash/Inerts	9.81	1.16	6.52
Ultimate Analysis (wt %, dry basis)			
Carbon	74.77	49.23	45.35
Hydrogen	5.08	5.93	5.75
Oxygen	6.32	43.27	40.24
Nitrogen	1.44	0.38	2.04
Sulfur	2.31	0.02	0.10
Chlorine	0.27	0.01	0.15
Ash/Inerts	9.81	1.16	6.52
Heating Value (Btu/lb)			
As-Received	11,748	5,431	7,108
Dry Basis	13,040	8,338	7,940
Moisture/Ash Free	14,457	8,437	8,494
Typical Moisture Content			
Weight Percent	10	40	10
Ash Analysis (wt %)			
SiO <sub>2</sub>	44.16	23.70	1.44
Al <sub>2</sub> O <sub>3</sub>	22.89	4.10	0.60
TiO <sub>2</sub>	1.00	0.36	0.05
Fe <sub>2</sub> O <sub>3</sub>	22.86	1.65	0.25
CaO	2.16	39.95	12.90
MgO	0.47	4.84	4.24
Na <sub>2</sub> O	0.25	2.25	0.61
K <sub>2</sub> O	1.97	9.81	40.53
P <sub>2</sub> O <sub>5</sub>	0.50	2.06	7.67
SO <sub>3</sub> <sup>-</sup>	1.93	1.86	1.60
Undetermined	1.81	9.43	17.44
Ash Fusibility			
Base/Acid Ratio	0.41	2.08	28.01
T <sub>250</sub> Temperature (°F)	2,397	2,440	---
Ash Fusion Temperatures (°F)			
Oxidizing Atmosphere			
Initial	2,406	2,546	> 2,700
Softening	2,545	2,563	> 2,700
Hemispherical	2,552	2,566	> 2,700
Fluid	2,565	2,577	> 2,700
Reducing Atmosphere			
Initial	2,082	2,274	> 2,700
Softening	2,273	2,577	> 2,700
Hemispherical	2,325	2,583	> 2,700
Fluid	2,429	2,594	> 2,700

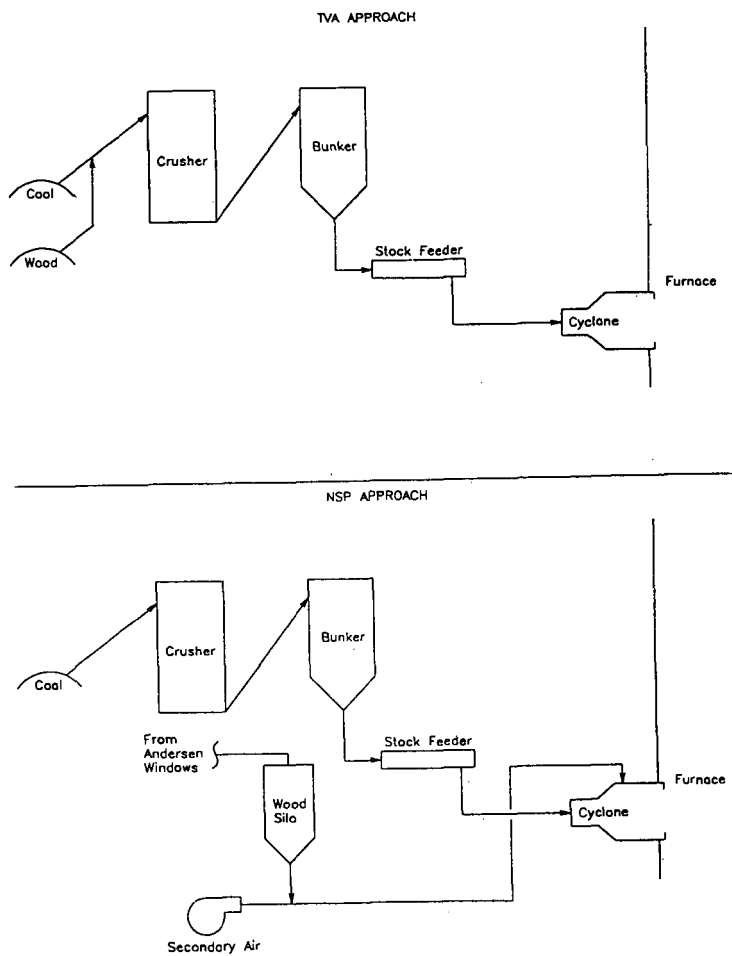


Fig. 1. Alternative Approaches to Cyclone Cofiring

## COFIRING WASTE BIOFUELS AND COAL FOR EMISSIONS REDUCTION

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**Keywords:** waste biofuels, coal, reburning, NO emissions

### ABSTRACT

Combustion tests have been performed in two pilot-scale combustion facilities to evaluate the emissions reduction possible while firing coal blended with several different biofuels. Two different boiler simulations, pulverized coal fired boilers and stoker coal fired boilers, were simulated. The pc-fired studies investigated the use of waste hardwood, softwood and sludge as potential reburning fuels and compared the results with coal and natural gas. The use of these wood wastes is attractive because: wood contains little nitrogen and virtually no sulfur; wood is a regenerable biofuel; wood utilization results in a net reduction in CO<sub>2</sub> emissions; and, since reburning accounts for 10-20% of the total heat input, large quantities of wood are not necessary. The results of this program showed that a reduction of 50-60% NO was obtained with approximately 10% wood heat input. Reburn stoichiometry was the most important variable. The reduction was strongly dependent upon initial NO and only slightly dependent upon temperature.

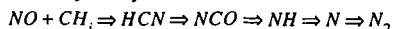
The stoker program investigated barriers for the successful blending of coal with waste railroad ties. Parameters evaluated included blending firing rate, chip size, optimum feed location, overfire/underfire air ratio, and natural gas addition. The results of this study demonstrated that NO emissions can be reduced by more than 50% without any significant increase in CO or THC emissions by the proper use of zoned reburning.

Both programs demonstrated several benefits of biofuel blends, including: 1) lower operating costs due to reduced fuel prices; 2) reduced waste disposal; 3) reduced maintenance costs; 4) reduced environmental costs; and 5) extension of the useful life of existing equipment.

### INTRODUCTION

Reburning is a combustion modification technology which removes NO<sub>x</sub> from combustion products by using fuel as the reducing agent. The concept was originally introduced by John Zink Company<sup>1</sup> and Wendt et al.<sup>2</sup>, based on the principle of Myerson et al.<sup>3</sup> that CH fragments can react with NO. Reburning is accomplished by secondary fuel injection downstream of the fuel-lean primary combustion zone. The second stage, or reburning zone is usually operated at overall fuel-rich conditions, allowing a significant fraction of the primary NO to be reduced to N<sub>2</sub> and other nitrogenous species. In the third zone, additional air is introduced to establish overall fuel-lean conditions and allow for the burnout of remaining fuel fragments.

Reduction of NO occurs primarily in the reburn zone by reaction of NO with hydrocarbon fragments (CH, CH<sub>2</sub>). These reactions typically produce hydrogen cyanide which decays in the reburning zone along the chemical pathway



This reburning concept is utilized in both experimental projects presented herein.

The waste biofuels that were tested include: pulverized hardwood and softwood waste from wood manufacturing, a wood-derived sludge, and chipped railroad ties. Discarded railroad ties represent a significant alternate energy resource and are available throughout the U.S. The wood manufacturing waste and wood-derived sludge materials are transportable but generally only available near the manufacturing locations. These and other similar products can be removed from the waste stream and can be significant alternative fuel sources. For example, approximately 16 million railroad ties are discarded or abandoned per year in the U.S., with a potential energy availability from RTDF of  $2 \times 10^{13}$  Btu/yr; equivalent to fueling a 350 MW power station.

Generally, the cost of these waste fuels is approximately 50 percent of coal on an energy basis. The wood-derived sludge is even less expensive, although its use may involve drying costs due to high moisture content (~65%). Although the cost incentive is apparent, the process parameters controlling the replacement of coal with biofuel wastes in boilers have not been defined. The purpose of these projects was to develop an understanding of the combustion of biofuels in conjunction with coal on stoker grates and in pc-fired boilers in order to define retrofit hardware that will allow replacement of coal and concurrent pollutant emissions reduction.

## APPROACH

Experiments were carried out in two facilities which are described below. Gaseous and solid samples were withdrawn from both furnaces at various locations. Gas samples were withdrawn through a water cooled, stainless steel probe, then filtered and dried. The gas sample was analyzed for NO (chemiluminescence), O<sub>2</sub> (paramagnetic), CO (NDIR) and N<sub>2</sub>O/NH<sub>3</sub> (FTIR). Temperatures are measured throughout each furnace with bare-wire, type-B thermocouples and a moveable suction pyrometer probe.

### Pilot Scale Spreader-Stoker

The pilot-scale spreader stoker facility, shown in Figure 1, is 3.2 m high and the stoker has a 0.09 m<sup>2</sup> grate. The furnace was designed to fire at rates from 126,000 to 252,000 kcal/hr. The base of the furnace provides support and houses the ash drawer. Air is injected under the grate and at various heights above the grate. Ports vertically located along the furnace allow for the addition of fuel and air for secondary burning. Coal was fed from the hopper via a metering auger to a rotating multi-vane spreader. Railroad ties were weighed into discrete predetermined quantities and fed into the stoker via the coal chute. The spreader is located 0.8 m above the bed and distributes the solid fuels uniformly across the bed. All of the furnace sections contain multiple ports for sample extraction, observations, and overfire air or natural gas injection. Three different stoker configurations were used: industrial, 2-U, and 2-N. In the 2-U configuration, overfire air was through the main gas burner ports and 2.2 m above the bed; reburning natural gas was injected 1.8 m above the bed. In the 2-N configuration, overfire air was added 1.8 and 3.2 m above the bed; natural gas was injected 2.2 m above the bed.

### Pilot Scale Pulverized Coal Furnace

Figure 2 shows the 38 kW, pulverized coal fired combustion research facility at the University of Utah. The main burner is located at the top left section and is down-fired. Access ports are available along the entire length of the furnace. The combustion chamber is 16 cm diameter and 7.3 m long and is constructed of composite refractory walls to minimize heat loss. The furnace is divided into three sections. The first section is the primary section where the main fuel burns at overall fuel-lean conditions. The second section is called the reburning section which begins at the point of injection of the reburn fuel (typically in the horizontal section of furnace as shown in Figure 2). The third section is the burnout section into which air is added to achieve overall fuel-lean conditions for burnout of the remaining fuel fragments.

Solid fuels were transported to the furnace by a transport fluid (usually air) which was laden with the solid fuel that was metered by a twin screw feeder. The feeder is a volumetric feeder with a variable speed motor that was calibrated for mass flow rates of each of the fuels tested.

## Objectives

The objectives of this paper are to report on experimental results which: 1) determine the feasibility of cofiring coal with waste biofuels, 2) compare the effectiveness of these fuels to natural gas in reburning, and 3) establish performance goals for the co-firing of coal and waste biofuels for emissions and waste reduction in both spreader-stoker and pc-fired boiler environments.

## RESULTS

### Stoker Experiments:

Initially, coal alone, and coal blended with hogged railroad ties were evaluated under typical industrial conditions where the overfire air was divided into two approximately equal segments above and below the spreader. Hogged railroad ties were fired with coal in an 80/20 coal/railroad ties ratio. Figure 3 presents the NO<sub>x</sub> and CO emis-

sions measured for these tests.

Under clean operating conditions (greater than 50 percent excess air and CO emissions less than 20 ppm), the  $\text{NO}_x$  emissions were lowered by about 30% with coal/railroad tie co-firing. This is likely due in part to the fact that the railroad ties contained essentially no nitrogen (0.22 percent).

The CO data (Figure 3) suggests that at low excess air levels the RTDF mix burns more completely. This is likely due to the presence of increased fines and the partially oxygenated nature of the wood fuel. The corresponding total hydrocarbon data for these fuels, tested at the commercial practice conditions, indicated there was little difference in the total hydrocarbon emissions for the co-firing case compared to the coal only case (the total hydrocarbon emissions were less than 20 ppm).

#### **Application of Low $\text{NO}_x$ Concepts - Reburning**

To evaluate the applicability of the low- $\text{NO}_x$  concepts described earlier, a series of co-firing experiments was conducted with 20 percent railroad ties in conjunction with natural gas addition. Figure 4 shows the  $\text{NO}_x$  and CO emissions for the RTDF/coal blend at an overall stoichiometric ratio of 1.28 and varying amounts of natural gas injection in the upper furnace. With 15 percent natural gas co-firing, the  $\text{NO}_x$  emissions were reduced to about 0.25 lbs  $\text{NO}_x$ /MBtu in this configuration and the CO was approximately 50 ppm. The baseline  $\text{NO}_x$  emissions were approximately 0.45 lbs/MBtu with a CO level of about 50 ppm for the coal only case. Also, CO concentrations decrease significantly with increased gas utilization.

The experience in this study suggests that a properly designed system could likely accommodate railroad tie feed rates higher than 20%. No problems with either bed slugging or other pollutant emissions were observed at the rates tested in this study. In a future test program, it would be desirable to investigate waste fuel firing rates up to 50 percent in this small scale unit to determine whether there are important scientific or practical reasons to limit the waste-fuel firing.

#### **PC-fired Experiments:**

Experiments conducted in the pc-fired facility (Figure 2) were performed without blending of the primary fuel with the waste biofuel. The biofuels were fired separately (and individually) in the reburning zone in each case.

##### **Reburn Stoichiometry**

The parameter that most dramatically influences the effectiveness of wood reburning is the stoichiometry in the reburn zone. The stoichiometric ratio (SR) in the reburn zone is determined by calculating the amount of oxidant required to convert all of the elements of the wood, the wood carrier, and the baseline products from the primary zone to carbon dioxide and water. Stoichiometric ratios less than 1 indicate fuel-rich conditions, while  $\text{SR} > 1.0$  indicates excess air conditions. Figure 5 presents the effect of reburn stoichiometry for reburning with hardwood at various temperatures. The variation in temperature was accomplished through movement of the position of the reburning zone in the furnace, with higher temperatures corresponding to reburn zones that are closer to the primary zone. In each of the cases the residence time in the reburn zone is held constant at about 400 ms. Notice that wood reburning is more effective at lower stoichiometries corresponding to increased wood reburning rate. The NO reduction achieved by hardwood reburning improves with increasing temperature as shown in Figure 5.

##### **Reburn Fuel Comparisons**

Figure 6 presents a comparison of hardwood, softwood, and wood sludge at the lower reburn temperature of 1398 K. The NO reduction achieved by the two wood types is very comparable except at stoichiometries less than 0.95 where the softwood performs slightly better than the hardwood. Each of the woods performs better than the wood sludge except at low stoichiometric ratios (0.85). A comparison of softwood, hardwood, wood sludge, coal and natural gas is presented in Figure 7 for the higher temperature reburning condition of 1721 K. At these high temperature conditions all of the fuels perform quite well leading to a reduction in NO of around 60% for  $\text{SR} \leq 0.9$ .

Figure 7 presents the very surprising result, that wood seems to reduce NO just as well as coal and natural gas at the high temperature reburn fuel injection condition of 1721 K. The wood sludge performs slightly worse except at low stoichiometries. This is surprising since wood is not expected to produce the same number of CH-radicals that



are required to begin the process of NO reduction to  $N_2$ . The similar performance of these fuels may be due to different factors, including possible enhanced mixing, and a delayed release of hydrocarbon species for the solid fuels compared to the natural gas. Although the fuels all seem to perform well as reburning fuels for the standard conditions investigated, they do not perform equally as well when NO levels into the reburning zone are lowered from 500 to 200 ppm, as indicated in Figure 8. For the case of only 200 ppm NO entering the reburn zone, wood and natural gas are significantly better reburning fuels than coal. This is most likely due to the increased nitrogen content of the coal (compared to the wood and gas).

## SUMMARY

These experimental studies have demonstrated that:

- 1)  $NO_x$  emissions can be reduced by more than 50 percent without any significant increase in CO or total hydrocarbon emissions by the proper use of natural gas in conjunction with appropriate tailoring of the stoichiometry distribution throughout the combustion zone in a pilot-scale stoker.
- 2) Railroad ties can be used as a co-firing fuel up to at least the 20 percent level without any detrimental effect on the pollutant emissions. Further, no combustion related operating problems were observed during the experimental studies.
- 3) To minimize overall  $NO_x$  emissions, one must control both the bed stoichiometry and the stoichiometry in the suspension phase combustion zone of a stoker.
- 4) Wood wastes (including a wood-derived sludge) can be used effectively as reburning fuels in a pc-fired furnace.
- 5) Reburn stoichiometry is the single most important parameter which determines the effectiveness of reburning with the waste biofuels, with optimal stoichiometric ratios around 0.85.
- 6) These biofuel waste streams can be utilized in a manner that reduces operating costs, and reduces environmental costs (including reductions in NO and CO emissions, and a net reduction in  $CO_2$  emissions) which makes them excellent candidates for practical application.

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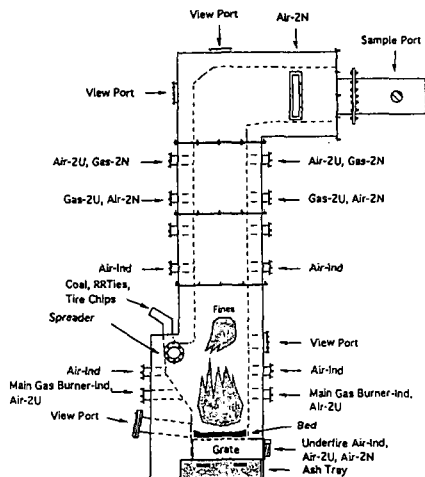


Figure 1. Pilot Scale Spreader-Stoker Facility.

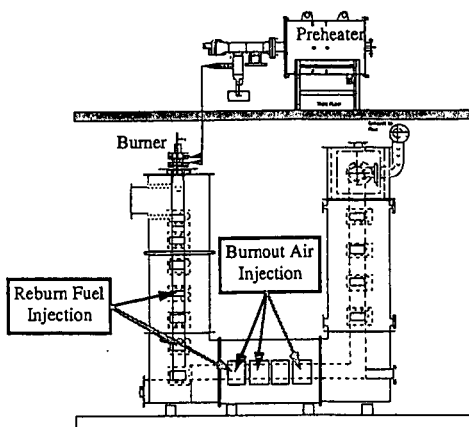


Figure 2. Pilot Scale Pulverized-Coal Fired Facility.

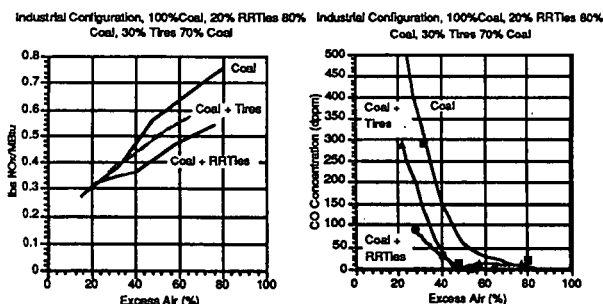


Figure 3. NO<sub>x</sub> and CO emissions for coal and coal/RTDF blend.

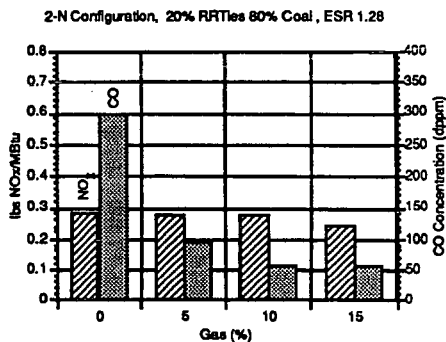
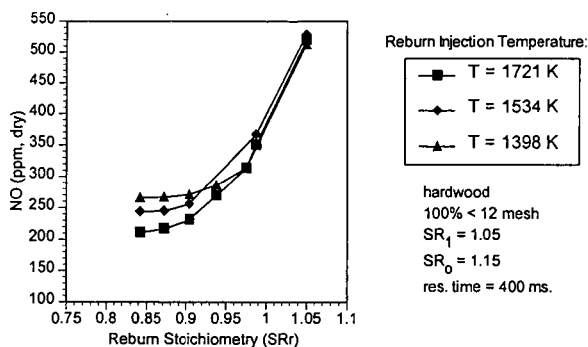
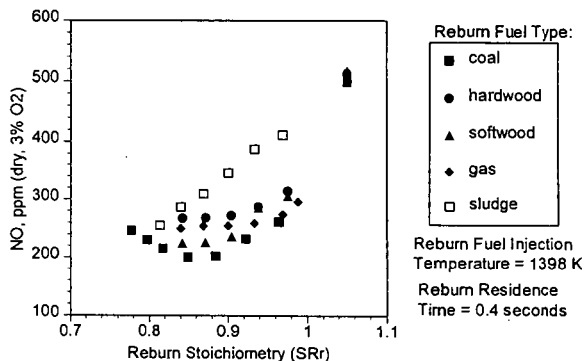


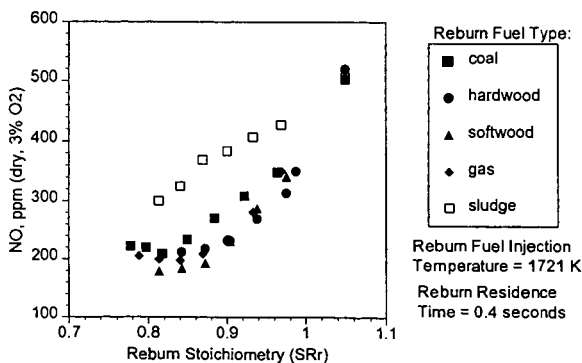
Figure 4. NO<sub>x</sub> and CO emissions for coal/RTDF blend with reburning.



**Figure 5.** Effect of reburn zone stoichiometry on NO emission for hardwood at three reburn fuel injection temperatures.



**Figure 6.** Reburn fuel comparisons at a reburn fuel injection temperature of 1398 K.



**Figure 7.** Reburn fuel comparisons at a reburn fuel injection temperature of 1721 K.

## CHARACTERIZATION OF COAL AND BIOMASS FUEL BLENDS

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Keywords: Fuel Characterization, Fuel Blending, Energy Generation

### ABSTRACT

The cofiring of biofuels with coal in existing boilers presents significant potential benefits to electric power generators. The practice has been shown to reduce  $\text{SO}_2$  and  $\text{NO}_x$  emissions, reduce fuel costs at some locations, and provide support to industrial customers from the forest products industry. One of the technical uncertainties associated with cofiring involves the characterization of the biomass and the coal, both separately and as fuel blends. Foster Wheeler Environmental Corporation has evaluated the practice of cofiring biomass with coal for the Electric Power Research Institute and the Tennessee Valley Authority. This paper reviews the characterization requirements and presents the analytical results for a number of coals and biomass wastes, focusing largely on the impact of fuel blending on ash fusibility and viscosity. Also, the consequences of these characteristics on the performance of pulverized coal and cyclone boilers is reviewed.

### INTRODUCTION

Foster Wheeler Environmental Corporation has been evaluating the practice of cofiring waste wood residues with coal at existing Tennessee Valley Authority (TVA) power plants for the Electric Power Research Institute (EPRI) and TVA. This work has been directed toward specific TVA power plants at cofiring levels up to 15 percent on a heat input basis. The following benefits can be expected from such a cofiring program:

- (1) A cost-effective program for reducing emissions of sulfur dioxide ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ );
- (2) A cost-effective strategy for reducing fossil fuel based carbon dioxide ( $\text{CO}_2$ ) emissions in concert with the global climate challenge of reducing the generation of greenhouse gases;
- (3) Potentially reduced cost of fuel to coal-fired power plants, improving their economics and consequent capacity utilization;
- (4) Increased support for the forest products industry in solving waste disposal problems.

The information presented here is focused specifically on cofiring waste wood residues with coal at the Allen Fossil Plant in Memphis, Tennessee and the Kingston Fossil Plant near Knoxville, Tennessee. The Allen Fossil Plant is equipped with three 265 MW cyclone boilers and has undergone parametric cofiring tests at low and moderate percentages of wood waste. The Kingston Fossil Plant is equipped with nine tangentially-fired pulverized coal boilers, four single furnace units rated at 136 MW<sub>e</sub> each, and five twin furnace units rated at 200 MW<sub>e</sub> each. The Kingston Fossil Plant has completed parametric testing of cofiring sawmill residues at low levels.

One of the technical uncertainties associated with wood cofiring lies in understanding the locally available fuels, with emphasis both on physical characteristics (particle size, specific gravity, and moisture content) and on fuel chemistry (proximate and ultimate analyses, higher heating value, and ash chemistry).

## CHARACTERISTICS OF LOCALLY AVAILABLE FUELS AND FUEL BLENDS

To characterize the locally available waste wood residues, over 25 potential wood fuel suppliers (including both sawmills and manufacturing facilities) in each of the Memphis and Knoxville areas were selected and sampled in the fall of 1993. Repeat sampling of ten of the sources from each area was completed in the spring of 1994. The sources of wood were characterized, including process flow diagrams for the processes that generated the wood waste. Wood samples were prepared and sent to a fuels laboratory for determination of the proximate analysis, ultimate analysis, calorific value, ash elemental analysis, and ash fusibility characteristics. Also, samples of coal from the Allen and Kingston Fossil Plants were sent to the laboratory for the same analyses. For the Allen Fossil Plant, blends of coal and wood were prepared on a dry weight basis at four levels (5, 10, 20, and 30 weight percent wood; these correspond to heat inputs of about 2.5, 5, 10, and 15 percent respectively). These samples also were sent to the laboratory for analysis. Particle size distributions for each wood fuel source were determined using a sieve analysis.

The direct result of this work is the detailed characterization of the various fuels and fuel blends. For both the Allen and Kingston Fossil Plants, these include the baseline coals, the locally available waste wood fuels, and blends of the coal and wood at various levels. The baseline coal and average wood fuel characteristics fell within expected ranges for these kinds of fuels. With regard to the variability in fuel characteristics for the wood fuels sampled, it was found that the statistical confidence intervals were relatively small. Consequently, it is expected that the average values presented are representative of the waste wood fuels available from these sources, and that relatively little variation from these values is expected. Such a stable, well-defined fuel characterization helps reduce the uncertainties associated with cofiring wood in coal-fired boilers. Tables 1 and 2 provide summary data concerning these analytical results.

The characteristics of coal and wood fuel blends can be seen largely as arithmetic averages of the characteristics of the two fuels. The more interesting exception to this generalization lies in the fusibility characteristics of the ash resulting from the fuel blends. A significant eutectic was present in the ash from the blends, reducing the ash fusion temperatures to levels below that of either fuel by itself. These results are depicted graphically as polynomial regressions of measured data in Figure 1.

## CONSEQUENCES FOR PULVERIZED COAL AND CYCLONE BOILERS

The issues of fuel characterization impact fuel handling, combustion, and ash management. From the perspective of fuel handling, the fine particle sizes obtained in the samples demonstrated that the fossil stations could avoid elaborate wood particle size reduction systems. Significant percentages of wood at  $<1/4"$ ,  $<1/8"$ , and  $1/16"$  document the fact that the materials handling system can consist of screens and magnets for pulverizer and boiler protection. Also, the materials handling system could include a wood fuel dryer, if desired. Extensive investments in hammer mills and related equipment can be avoided by procurement practices. Further, the wood moisture contents will likely be on the order of 40 to 50 percent, based upon the experience of the sampling teams in the field.

The characterizations of the fuel lead to assessments of their impact on boiler performance at cofiring levels of 10-15 percent (heat input basis). Such characterizations lead to the conclusion that, at operating conditions currently associated with the Allen and Kingston facilities, there would be no significant deleterious impact on boiler efficiency or net station heat rate. Similarly, there is no significant impact on flame temperatures.

Of more consequence is the impact on ash chemistry and the behavior of non-combustibles, particularly as it relates to the cyclones.

The reduction in the ash fusion temperatures associated with fuel blends is consistent with the fact that the Base/acid ratio is increased relative to that of the coal used at the Allen Fossil Plant, and decreased relative to that of the wood available in the Memphis area. The resulting base/acid ratio associated with the blends approaches 1.0 from both "pure fuel" directions.

This analysis does not, and can not address the impact of fuel blending on the final ash consideration: the salability of flyash as a pozzolanic material, or the sale of slag for such products as roofing granules. Those questions can only be addressed by significant additional testing of the cofiring process.

In conclusion, the fuel characterization studies demonstrated the significant potential associated with cofiring. The wood fuels available to Allen and Kingston Fossil Plants are not unusual, and contain no significant problems.

ACKNOWLEDGMENTS

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Figure 1: Ash Fusion Temperatures for Coal/Wood Fuel Blends  
 Ash Fusion Temperatures (Oxidizing) for Allen Fossil Plant Fuel Blends

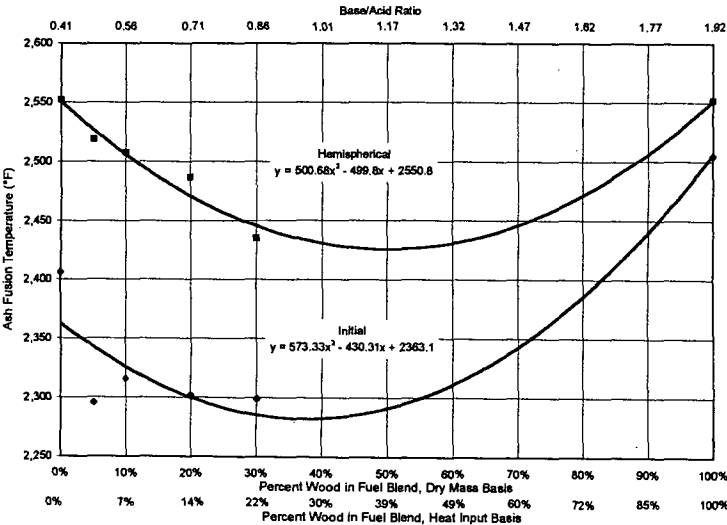


Table 1: Summary of Coal Characterizations

Parameter	Allen Coal	Kingston Coal
Proximate Analysis (wt %, as rec'd)		
Moisture	9.91	7.17
Volatile Matter	33.53	33.78
Fixed Carbon	47.73	49.06
Ash/Inerts	8.83	9.99
Ultimate Analysis (wt %, dry basis)		
Carbon	74.77	74.35
Hydrogen	5.08	5.02
Oxygen	6.32	7.19
Nitrogen	1.44	1.52
Sulfur	2.31	1.14
Chlorine	0.27	0.02
Ash/Inerts	9.81	10.76
Heating Value (Btu/lb)		
As Received	11,748	12,378
Dry Basis	13,040	13,334
Moisture/Ash Free	14,457	14,814
Ash Elemental Analysis (wt %)		
SiO <sub>2</sub>	44.16	47.66
Al <sub>2</sub> O <sub>3</sub>	22.89	23.05
TiO <sub>2</sub>	1.00	0.75
Fe <sub>2</sub> O <sub>3</sub>	22.86	19.08
CaO	2.16	2.37
MgO	0.47	0.93
Na <sub>2</sub> O	0.25	0.56
K <sub>2</sub> O	1.97	2.43
P <sub>2</sub> O <sub>5</sub>	0.50	0.43
SO <sub>3</sub> <sup>-</sup>	1.93	2.13
Undetermined	1.81	0.61
Alkali Metals (lb/MMBtu)		
CaO	0.15	0.18
MgO	0.03	0.07
Na <sub>2</sub> O	0.02	0.04
K <sub>2</sub> O	0.13	0.18
Ash Fusion Temperature (°F)		
Oxidizing Atmosphere		
Initial	2,406	2,481
Softening	2,545	2,528
Hemispherical	2,552	2,535
Fluid	2,565	2,553
Reducing Atmosphere		
Initial	2,082	2,081
Softening	2,273	2,300
Hemispherical	2,325	2,418
Fluid	2,429	2,444
T <sub>250</sub> Temperature (°F)	2,397	2,463
Base/Acid Ratio	0.41	0.36
Slagging Index	0.94	0.40
Fouling Index	0.10	0.2

Table 2: Summary of Wood Fuel Characterizations

Parameter	Allen Wood		Kingston Wood	
	Average	95% Conf. Interval	Average	95% Conf. Interval
Proximate Analysis (wt %, dry)				
Volatile Matter	84.32	0.70	84.85	0.65
Fixed Carbon	14.47	0.55	14.45	0.59
Ash/Inerts	1.21	0.47	0.70	0.16
Ultimate Analysis (wt %, dry)				
Carbon	49.24	0.21	49.81	0.31
Hydrogen	5.90	0.05	5.96	0.08
Oxygen	43.24	0.42	43.18	0.35
Nitrogen	0.39	0.27	0.32	0.21
Sulfur	0.02	0.00	0.02	0.00
Chlorine	0.01	0.01	0.01	0.01
Ash/Inerts	1.21	0.47	0.70	0.16
Heating Value (Btu/lb)				
Dry Basis	8,335	38	8,391	46
Moisture/Ash Free	8,437	34	8,450	45
Ash Elemental Analysis (wt %)				
SiO <sub>2</sub>	22.90	5.29	17.93	4.05
Al <sub>2</sub> O <sub>3</sub>	4.43	1.11	4.55	1.16
TiO <sub>2</sub>	0.46	0.48	0.78	1.04
Fe <sub>2</sub> O <sub>3</sub>	1.79	0.45	1.96	0.39
CaO	40.16	3.77	39.89	3.71
MgO	5.37	1.22	8.12	2.07
Na <sub>2</sub> O	2.93	1.45	2.74	2.04
K <sub>2</sub> O	9.48	1.78	10.33	1.81
P <sub>2</sub> O <sub>5</sub>	2.25	0.38	3.42	1.55
SO <sub>3</sub>	2.07	0.91	2.08	0.58
Undetermined	8.16	---	8.20	---
Alkali Metals (lb/MMBtu)				
CaO	0.58	---	0.33	---
MgO	0.08	---	0.07	---
Na <sub>2</sub> O	0.04	---	0.02	---
K <sub>2</sub> O	0.14	---	0.09	---
Ash Fusion Temperature (°F)				
Oxidizing Atmosphere				
Initial	2,517	90	2,472	47
Softening	2,538	87	2,526	27
Hemispherical	2,541	88	2,530	22
Fluid	2,553	94	2,534	19
Reducing Atmosphere				
Initial	2,541	128	2,537	182
Softening	2,552	134	2,546	193
Hemispherical	2,558	128	2,549	191
Fluid	2,568	117	2,557	181
T <sub>250</sub> Temperature (°F)	2,424	75	2,384	105
Base/Acid Ratio	2.15	---	2.71	---
Slagging Index	0.04	---	0.05	---
Fouling Index	6.30	---	7.43	---



## CO-PROCESSING OF AGRICULTURAL AND BIOMASS WASTE WITH COAL

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Keywords: Co-liquefaction, Sawdust, Manure, Coal

### INTRODUCTION

A major thrust of our research program is the use of waste materials as co-liquefaction agents for the first-stage conversion of coal to liquid fuels. By fulfilling one or more of the roles of an expensive solvent in the direct coal liquefaction (DCL) process, the waste material is disposed off ex-landfill, and may improve the overall economics of DCL. Work in our group has concentrated on co-liquefaction with waste rubber tires, some results from which are presented elsewhere in these Preprints. In this paper, we report on preliminary results with agricultural and biomass-type waste as co-liquefaction agents.

The ideal co-liquefaction agent has, at a minimum, three characteristics: it should be available in an unlimited supply; it should be expensive to dispose of, whether in a landfill or by other means; and it should contain components which can function as hydrogen-transfer agents and/or termination agents for free radicals. The first two of these allow for a significant economic impact on the DCL process, and the last ensures good processing properties. While no single agent fulfills all these requirements, the two categories used in the present work are viable candidates. In the category of biomass-type waste, we have used sawdust. In the category of agricultural waste, we have used horse manure, cow manure, and a more-prosaic (but perhaps more-reproducible) commercially available manure ("Supermanure").

All of these agents contain varying amounts of the following components: extractables (oils), cellulose, hemi-cellulose, lignin and ash. Typically, extractables can be removed by a simple water extraction. The insolubles, when extracted with concentrated HCl, yield a soluble cellulose/hemicellulose portion. The HCl-insoluble when subjected to NaOH extraction, yield lignin as the soluble phase while ash is classified as NaOH- (and HCl-) insoluble. Cellulose and hemi-cellulose have a more-or-less well defined structure, with six-membered rings of  $-C_6H_5O(OH)_2CH_2OH$  linked with  $-O-$ . The structure of lignin is much less defined, but is known to contain building blocks of phenylpropane with  $\alpha$ -alkyl ether linkages and/or  $\beta$ -4' ether linkages. Breakage of these linkages may well involve DCL-solvent-like properties.

### EXPERIMENTAL

Standard tubing-bomb reactors were used. They were filled with either coal alone or equal weights of coal and one of the co-liquefaction agents described above. The coal used throughout these runs was a high-volatile-A bituminous coal from the Blind Canyon seam, Utah, coded as DECS-6 by the Pennsylvania State University Coal Bank. The coal was ground to -60 mesh under nitrogen. For consistency with previous work, a small amount of sulfiding agent (0.1 ml  $CS_2$ ) was added to all run batches. Reactions were carried out both in the absence of any additional solvent and with 5 ml of tetralin. Standard reaction conditions were used: 1000 psi (cold) hydrogen, 350°C, vertical agitation at 500 cpm, 1 h. After the reaction, the total conversion (of all solids) and the yields of asphaltene and preasphatene and oil+gas were obtained by solution of the remaining solids in tetrahydrofuran and n-hexane. Additional details can be found in e.g. [1]. Runs were repeated at least once. The reproducibility is typically 2%.

## RESULTS AND DISCUSSION

Results for the co-liquefaction of DECS-6 coal and sawdust are summarized in Table I. Liquefaction results of the sawdust alone are significantly greater than those of the coal alone. The addition of tetralin improves the coal-alone results considerably, especially the yield of asphaltene+preasphaltene. The "DIFFERENCE" entries refer to the improvement (if positive) in the results of coal plus sawdust runs, relative to the average of the individual coal and sawdust runs. In the absence of tetralin, there is an improvement in the oil+gas yield at the expense of the asphaltene+preasphaltene yield, while the improvement in the total conversion is within experimental limits. These results indicate that sawdust may catalyze the formation of asphaltenes to oils or may cap low-molecular-weight radicals or other species to prevent retrograde formation of asphaltenic products by combination of oil-range products. The former appears to be unlikely in the light of the results with tetralin: in conversion and yields, there is negligible difference between the individual coal and sawdust runs and the coal-plus-sawdust run. Clearly, the sawdust under liquefaction conditions acts more as a solvent than a catalyst; when tetralin, a powerful solvent, is present, its effect overwhelms that of sawdust. Finally, it is interesting to note that the oil+gas yield after the run with sawdust plus coal is undistinguishable from that when tetralin is also added. Hence, the effects of 5 ml tetralin can be suitably substituted for by 3 g of sawdust. This is obviously of great economic importance.

Results with "Supermanure" are shown in Table II. As in Table I, the co-liquefaction agent alone shows greater conversion and oil+gas yield than coal alone, and the addition of the tetralin has a much smaller effect on the co-liquefaction agent alone than on the coal alone. In the absence of tetralin, the addition of "Supermanure" to the coal increases the oil+gas yield but decreases the overall conversion. Both changes are slight, but significant. In the presence of tetralin, the addition of "Supermanure" to coal appears to decrease the oil+gas yield fairly substantially and also decreases the total conversion slightly. This is a different effect than that observed in Table I. Clearly the constituents of sawdust and "Supermanure" are different, and this is manifested in the behavior when tetralin is present.

Table III summarizes the behavior of cow manure as a co-liquefaction agent. Acting alone, this agent is not liquefied as readily as "Supermanure" and does not yield as much oil+gas fraction. However, in the presence of coal, with or without tetralin present, there is a significant difference (improvement) in oil+gas yield, and this is achieved at the expense of the asphaltenic fraction.

Finally, we indicate in Table IV the effect of horse manure as a co-liquefaction agent. In the absence of tetralin, the presence of horse manure significantly improves the total conversion, and that difference is manifested almost entirely in the oil+gas yield. In the presence of tetralin, the difference in total conversion after adding horse manure is even larger, but that difference is manifested to a large extent in improving the asphaltenic yield. The total conversion and the yield of asphaltenic+preasphaltenic fractions are significantly increased when tetralin is added; the oil+gas yield is also increased but to a lesser extent. Clearly the effect of horse manure is not just to act as a substitute for a more-expensive solvent; there may well be some catalytic effects involved.

The temptation to ascribe the differences in behavior of manure from the horse and cow to differences in the diet of these two species is strong. However, we have not yet carried out analyses of these two co-liquefaction agents to test our hypothesis.

## CONCLUSIONS

In the absence of tetralin, the total conversion of equal parts of

coal and a co-liquefaction agent is approximately equal for sawdust, "Supermanure" and horse manure; the value for cow manure is somewhat smaller. However, the greatest improvement (over the conversion of individual reactants) occurs for horse manure; the conversion for "Supermanure" is significantly smaller than the sum of the individual values. The absolute values of the oil+gas yields follow the same trends as those observed for the total conversions; and the improvement of this yield (over yields of individual reactants) also follows the same trends as the improvement of the total conversions.

In the presence of tetralin, both the absolute value of the total conversion and the improvement over conversions of individual species are observed for horse manure as the co-liquefaction agent. The total conversion is almost doubled when tetralin is present, relative to the value in the absence of tetralin, the absolute values of the oil+gas yield are somewhat greater for horse manure and for sawdust than for the other two. Interestingly, the greatest difference, i.e., improvement over individual oil+gas yields, is observed for the case of cow manure as the co-liquefaction agent. In fact, all other improvements in oil+gas yields are either negligible or negative.

Hence the use of biomass-type and agricultural waste as agents of co-liquefaction of coal is in general worthy of consideration.

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#### ACKNOWLEDGMENTS

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**TABLE I**  
**Results for Sawdust/Coal Co-Liquefaction**

Sawdust	Coal	Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	No	22.4	17.3	5.1
Yes	No	No	70.4	7.7	62.7
Yes	Yes	No	47.6	8.7	38.9
(DIFFERENCE)		No	+1.2	-3.8	+5.0
No	Yes	Yes	57.0	50.0	7.0
Yes	No	Yes	93.1	28.5	64.5
Yes	Yes	Yes	74.7	38.2	36.5
(DIFFERENCE)		Yes	-0.3	-0.8	+0.5

**TABLE II**  
**Results for "Supermanure"/Coal Co-Liquefaction**

Supermanure	Coal	Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	No	22.4	17.3	5.1
Yes	No	No	80.0	18.0	62.0
Yes	Yes	No	48.2	11.9	36.3
(DIFFERENCE)		No	-3.0	-5.8	+2.7
No	Yes	Yes	57.0	50.0	7.0
Yes	No	Yes	87.4	23.5	63.9
Yes	Yes	Yes	69.6	38.4	31.2
(DIFFERENCE)		Yes	-2.6	+1.6	-4.3

TABLE III  
Results for Cow-Manure/Coal Co-liquefaction

Cow Manure	Coal Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	22.4	17.3	5.1
Yes	No	57.4	17.8	39.6
Yes	Yes	39.8	12.2	27.6
(DIFFERENCE)	No	-0.1	-5.4	+5.2
No	Yes	57.0	50.0	7.0
Yes	Yes	66.9	17.7	49.2
Yes	Yes	62.1	29.2	32.9
(DIFFERENCE)	Yes	-0.1	-4.7	+4.8

TABLE IV  
Results for Horse-Manure/Coal Co-liquefaction

Horse Manure	Coal Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	22.4	17.3	5.1
Yes	No	66.2	13.4	52.8
Yes	Yes	48.2	14.4	33.8
(DIFFERENCE)	No	+3.9	-1.0	+4.8
No	Yes	57.0	50.0	7.0
Yes	Yes	88.2	22.1	66.1
Yes	Yes	81.5	43.4	38.1
(DIFFERENCE)	Yes	+8.9	+7.3	+1.5

## STUDIES IN COAL/WASTE COPROCESSING AT HYDROCARBON RESEARCH, INC.

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**Keywords:** Waste Recycling, Catalytic Coprocessing, Co-Liquefaction

**ABSTRACT:** - The co-liquefaction of waste plastics with coal and waste tire rubber with coal was successfully demonstrated at a combined processing rate of 3 TPD at the Proof-of-Concept facility of Hydrocarbon Research, Inc. in Lawrenceville, N.J. The POC Program is jointly funded by the U.S. DOE, Hydrocarbon Research, Inc., and Kerr McGee Corporation. A total of 12 tons of plastics & coal and 5 tons of waste rubber tire & coal were processed to produce clean light distillates (IBP-343°C) with less than 40 ppm of nitrogen and 20 ppm of sulfur. Coal conversion was well maintained (92 W% maf) and nearly complete conversion of the organic waste to oils was achieved (65 W%+ maf distillate yields). Both the plastics and rubber contributed hydrogen to the liquefaction thereby reducing the hydrogen consumption by as much as 2 W% of the maf feed. This has a direct impact on reducing the cost of premium fuels from coal. Co-liquefaction of waste organic materials with coals provides for the recovery and recycle of waste materials back into the economy as premium fuels and feedstocks for petrochemicals. A concerted effort is underway to optimize the process to produce more value-added products with improved energy efficiency.

**INTRODUCTION:** - Increasing problems associated with waste disposal, combined with the recognition that some raw materials may exist in limited supply, dramatically increase interest in recycling. Recycling of paperboard, glass, and metal are well understood and these materials are now recycled in many areas around the world. Recycling of plastics presents greater technical challenges<sup>(1)</sup>, primarily due to the differences in the chemical compositions/properties of various types of plastics. Used automobile tires, the main source of waste rubber, pose another environmental challenge. Most of the 200 million used tires that are discarded in the United States every year, end up in stockpiles or landfills, although recently some use of scrap tires is also reported as fuel for power generation. Other reported methods of recycling the scrap tires are based on pyrolysis which results in low thermal efficiency and also poor selectivity to liquid fuels.

**RATIONALE:** - Coal is an abundantly available fossil fuel source with low hydrogen contents. The cost of hydrogen is a significant portion of the total cost of converting coal to refined transportation fuels such as gasoline, kerosene, and diesel via the state-of-the-art conversion technology. These municipal solid waste components such as plastics or hydrocarbon oil in used tires are relatively richer in hydrogen contents than coal. Thus, using these as a part of the feed in coal liquefaction would significantly reduce the cost of hydrogen production. There also seems to be a distinct advantage in processing plastics/rubber waste in a liquid phase or slurry mode under conditions much milder than those used in pyrolytic methods of conversion. Coal as a component of the feed mixture can thus provide not only a way to liquefy these waste stream, but can also act as a "mitigator" in maintaining the overall composition/properties of the combined feedstocks more uniform. This mediator role of coal is very crucial for any waste-stream conversion/recycling process because the waste streams, depending on location, are going to be inherently different in their compositions. Thus, it appears to be practical to co-process the most abundantly available fossil fuel, coal, with hydrogen-rich, though inhomogeneous in composition/properties, waste streams. Feed mixtures consisting of between 20-40 W% wastes (esp. plastics) are considered realistic and are being studied for catalytic slurry processing at Hydrocarbon Research, Inc. For used rubber tires, co-processing with coal can provide a better way for disposal while the carbon black component of the tires is reported to provide catalytic action during coal conversion reactions<sup>(2)</sup>.

**LABORATORY-SCALE WORK:** - Initial work carried out at Hydrocarbon Research, Inc., to a large extent, was a follow up of the research reported by the Consortium of Fossil Fuel Liquefaction Science<sup>9</sup>. It mainly constituted some microautoclave testing for the screening of the plastics feedstocks reactivity, process severity required, and the catalyst additive for plastics depolymerization. The lab-scale work focused primarily on the pure plastics, i.e., HDPE, Polystyrene, and PET, in the extrudate form. No lab-scale work was carried out in support of the coprocessing of used tire rubber with coal as HRI had a past experience in handling crumb rubber slurries from its H-Rubber process-related work. Our dissolution experiments with mixed plastics indicated that plastics (in coal/petroleum derived oil), especially HDPE, needed about 30-45 minutes at temperatures in excess of 220°C for complete dissolution. Adding coal to this plastics/oil mixture appeared to influence the fluidity of the total slurry in a positive way. The pre-mixed coal, plastics, and oil slurries at 33 and 50 W% of mixed plastics in solid feed exhibited a good pumpability behavior and when tested for reactivity in the 20 CC microautoclave at 440°C and 60 minutes reaction time, about 92 W% conversion to THF soluble products was obtained. Of the three plastics we tested individually at the lab-scale, HDPE was found hardest to convert while both the polystyrene and the PET converted almost completely under coal liquefaction condition.

**PDU-SCALE EXPLORATORY WORK:** - As a part of the US DOE sponsored Proof-of-Concept (POC) direct coal liquefaction program, the technical and operational feasibility of co-liquefaction of coal and plastics/rubber tire wastes was evaluated at a 3.0 TPD scale. A schematic of the HRI's PDU facility is shown in Figure 1. An eight day long extension of the PDU run POC-02 was carried out using Wyoming subbituminous coal from Black Thunder mine and pure forms of high density polyethylene, polystyrene, polyethylene terephthalate, and -20 mesh crumb tire rubber in a two-stage catalytic mode of operation, with an in-line hydrotreater. During the first six days, a total of 12 tons of mixed plastics were processed with coal (@30% plastics), while 5 tons of fiber-free -20 mesh crumb rubber tire (@26% of solid feed) was processed with coal during the last two days of continuous operation. The coal/waste feed was prepared in two steps: rubber/plastic waste was first slurried with recycle solvent and transferred to the slurry mix tank to which coal and more recycle solvent were added. It was found that a recycle solvent-to-solid feed ratio of about 2.25 was satisfactory for smooth pumping operations with plastics/rubber wastes. Some foaming problems were encountered at the slurry mix tank because of its high temperature and high moisture content of the feed coal. Table 1 contains detailed operating conditions. Because of the fact that the co-liquefaction operation/extension of the PDU run POC-02 was of short duration, the time allowed for process equilibration was not sufficient. As a result of this, the results obtained and presented in Table 2 should be considered with caution; also it should be viewed as directional data rather than an absolute performance during co-liquefaction. Table 2 compares the performance of the "coal-only" feed Period 36 with two coal-plastics cases (Periods 42 & 43) and one coal-rubber case (Period 45). The mixed plastic feed contained 50% HDPE, 35% PS, and 15% PET, simulating the compositions in a typical municipal solid waste. It can be seen from Table 2 that co-liquefaction resulted in a reduced hydrogen consumption, while maintaining total coal and resid conversions. The distillate liquid yields were also higher. The quality of the distillates obtained during the co-liquefaction periods was also premium with very low nitrogen and sulfur contents (Figure 2). Due to the overall process severity and short duration for the entire operation, a steady-state with respect to the recycle solvent was not achieved, i.e., significant portions of an external make-up oil had to be used to obtain a solvent/coal ratio of 2.25 (Figure 3). As a result, light fractions of the make-up oil were excessively hydrocracked increasing the yield of light gases. Some degradation of heavy co-liquefaction products was also noticed across the solids-separation Vacuum Tower/ROSE-SR systems.

**BENCH-SCALE WORK:** As a follow-up of the exploratory PDU scale test of co-liquefaction, a bench test is being conducted to delineate the effects of process severity, catalysis, feed composition during coal/plastics co-processing, when process is at steady-state and is under complete solvent-balance. The same mixture of co-mingled plastics, used earlier at the PDU scale, and Illinois No.6 Crown II mine coal is being evaluated in a 20 Kg/Day two-stage bench-scale unit. Preliminary results confirm our earlier findings at the PDU level. The process is being operated in a catalytic/thermal mode with sulfated iron-molybdenum dispersed catalyst only in stage II. For the first 14 days of this operation so far, solvent-balance conditions have been achieved. Preliminary results are about 6-8% gas yields, 71-73% distillate liquid yields, and 6-7% hydrogen

consumption (all on maf basis) result from co-liquefaction at the overall process severities lower than that at the PDU scale. The final results of this work will be conferred at the meeting.

**SUMMARY:** - Overall co-liquefaction operations at the PDU scale were successful and established both the technical and operational feasibility of the process. In general, high total (coal+plastics/rubber) conversions were obtained with high resid conversions; the yield of light distillates was high and distillates were of high quality (high H/C, very low N & S contents). We were also successful at establishing a procedure for preparation and pumping under high pressure of the feed materials that contain as much as 26 W% co-mingled plastics and/or crumb rubber. It is well understood that since insufficient time was allowed for the equilibration of the process, recycle solvent-balance was never achieved any time during the operations. The problem of solvent-balance maintenance during continuous operations is being currently addressed at bench-scale. Our ongoing work addresses all the above issues such as optimum process severity, catalysis, solvent balance, and process equilibration. The final results of our latest work in this area will be discussed during the final paper.

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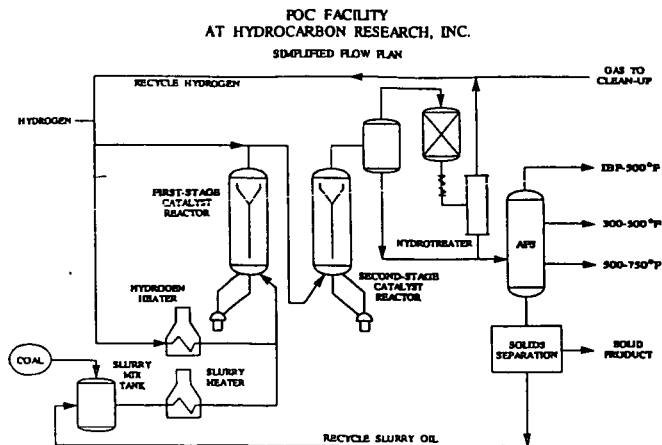


Figure 1



# Inspection of Naphtha Stabilizer Bottom SULFUR & NITROGEN REMOVAL

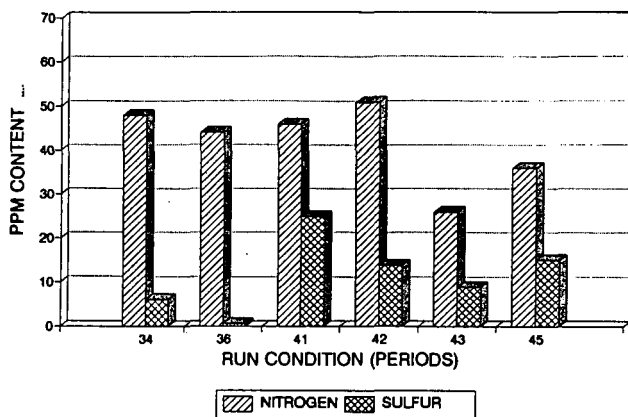


Figure 2

# POC-02 PDU RUN 260-005 RECYCLE STREAM COMPOSITION

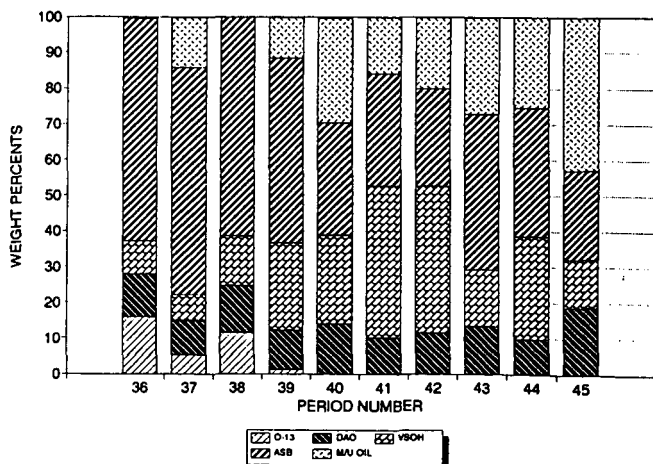


Figure 3

**Table 1. Operating Summary During Co-Liquefaction**

Process Conditions	5	6	6	7
Period/s	Rose-SR 35-36	Rose-SR 42	Rose-SR 43	Rose-SR 45
Recycle Type	Ashy	Solids-free	Solids-free	Solids-free
Feed*, Wt%:				
Coal	100.00	88.00	70.00	74
Plastics (42,43) & Rubber (45)	0.00	32.00	30.00	26
HDPE	n/a	19	15	n/a
PS	n/a	13	10	n/a
PET	n/a	0	5	n/a
Ground Rubber	n/a	n/a	n/a	26
Space Velocity, Kg/hr/m3	814.50	379.00	433.80	398.40
K-1:				
Temperature, Deg. C	432.20	428.30	431.10	430.00
Cat Replac. Rate, Kg/Kg Ton MF Coal	0.75	0.45	0.45	0.00
Catalyst Age, Kg MF Coal/Kg Cat	1026.00	1044.00	1056.00	1072.00
K-2:				
Temperature, Deg. C	443.50	442.80	443.80	442.80
Cat Replac. Rate, Kg/Kg Ton MF Coal	1.25	0.90	0.90	0.00
Catalyst Age, Kg MF Coal/Kg Cat	626.00	632.00	641.00	660.00
<b>Flow Rates</b>				
Coal Feed, Kg/hr	139.40	80.00	88.80	66.40
Plastics/Rubber	0.00	29.24	29.50	23.30
Oil Streams to SMT				
O-43 Recycle to SMT, Kg/hr	87.85	103.50	64.68	71.56
Make up Oil, Kg/hr	0.00	40.00	58.53	93.52
ASB (thru' COT) to SMT, Kg/hr	108.85	55.87	96.20	54.49
Solvent/Coal Ratio, Kg/Kg	1.30	2.26	2.24	2.45

**Table 2. Process Performance During Co-Liquefaction**

**Material & Ash Balances**

Liquefaction Section Recovery, Wt%	100.10	97.10	97.70	99.70
Overall Material Recovery, Wt%	99.35	97.80	100.30	98.80
Normalization Factor	1.00	1.03	1.02	1.00
Ash Balance, Wt%	103.70	118.99	108.90	116.44

**NORMALIZED YIELDS, Wt% MAF FEED\***  
[Based on Liquefaction Section: O-13 Bottoms]

H2S	0.56	1.61	1.25	2.25
NH3	1.03	0.66	0.63	0.86
H2O	19.28	14.72	18.56	16.30
COx	1.16	0.49	0.90	0.85
C1-C3	10.11	14.39	10.28	11.54
C4-C6	4.50	7.77	4.17	6.61
IBP-177 C	18.28	27.81	22.04	22.05
177-268 C	24.91	36.31	31.08	40.16
268-343 C	1.32	15.39	15.94	24.27
343-524 C	8.42	-22.82	-3.73	-26.92
524 C+	12.01	-0.42	0.10	3.79
Unconverted Coal	8.51	7.20	7.20	5.32

**PROCESS PERFORMANCE (Combined Feed Basis)**

Chemical H2-Consumption, Wt% MAF	8.05	8.34	8.50	7.47
Total Feed Conversion, Wt% MAF	93.50	92.80	92.80	94.68
524 C+ Conversion, Wt% MAF	81.50	93.20	92.70	90.90
Denitrogenation, Wt%	88.25	77.40	78.00	74.60
C4-343 C Net Distillates, Wt% MAF	49.00	90.30	73.20	93.10
C4-524 C Distillates, Wt% MAF	57.50	67.70	69.50	66.20
C1-C3 Selectivity, Kg/Kg of C4-524 C (X 100)	17.80	21.30	14.80	18.00
H2 Efficiency, Kg C4-524 C/Kg H2	7.16	10.70	10.70	8.90
Deasher Coal Conversion, Wt% MAF	90.9	79.00	85.50	85.50

\*"Fresh Feed" is a combination of coal and plastics or coal and crumb rubber for Periods 42,43, & 45;

## THERMAL PROCESSING OF UNUSED WASTE PRODUCTS; THE SASOL PERSPECTIVE

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**Keywords:** Co-processing, waste, gasification

### 1. INTRODUCTION

The Sasol group of companies gasify approximately  $28 \times 10^6$  metric tons of coal in their 97 Lurgi fixed bed gasifiers per annum. The syngas produced is used mainly in their Fischer-Tropsch plants for the production of transport fuels as well as a slate of other chemicals.

In a complex operation such as Sasol, various sources of unutilized products or waste exist. Tars produced during gasification contain a substantial amount of solid material, essentially fine char and ash. Through various steps of sedimentation and filtration most of the tar is recovered as a clear liquid ready for further work-up. However an amount of "dusty tar", high in solids (MIQ) is produced. In the operation of the Synthol (Fischer Tropsch) reactors, fine catalyst is carried over in the liquid product. This is also concentrated to form a waste product high in finely divided catalyst. Like any other large petrochemical facility from time to time waste from a number of sources is produced down-stream. Where re-working is not feasible, the material has to be disposed of.

In the 40 years of operation of Sasol One (now called Sasol Chemical Industries or SCN) as well as the approximately 15 years of operation of the Sasol Two and Sasol Three facilities (now collectively called Sasol Synthetic Fuels or SFF) substantial amounts of these unused products or wastes have been dumped in ponds. In the early days of the SCN operation, dumping was done rather ad-hoc in waste ponds which were not lined. In later years, properly lined disposal ponds were constructed. The SFF facilities were equipped with properly lined ponds from start-up.

In line with world trends, Sasol has adopted a stringent environmental policy and dumping of such materials is no longer acceptable. Furthermore, Sasol is signatory to the Responsible Care Program. It is now the official policy of the company, not only to eliminate dumping but also to clean up existing waste in an environmentally acceptable way. Thermal co-processing with coal has been identified as a means by which such waste can be upgraded to liquid and gaseous product with no additional toxic effluent.

## **2. THERMAL CO-PROCESSING WITH COAL: DEFINITION AND OPTIONS IN THE SASOL CONTEXT**

Co-processing of waste with coal has to be compatible with the Sasol operations and business scenario. The often heterogeneous feed may not affect the integrity of Sasol operations. Furthermore, it is desirable that products, whether gaseous, liquid or solid are such that they can be upgraded in existing refining facilities and be compatible with products which are currently being marketed. No new toxic waste products are acceptable. Within the limitations of these requirements, Sasol has two options in terms of thermal co-processing of waste with coal: The use of existing fixed bed gasifiers or a dedicated reactor (Figure 1).

### **3 GASIFICATION**

The 97 Lurgi gasifiers currently in operation offer an opportunity for co-processing waste with the existing coal feed. It makes economic sense in that it would significantly reduce the capital outlay needed otherwise. There is the further advantage that gas, liquid and solid products will be "automatically" worked away in the existing infrastructure, again saving on capital investment. Gases produced would end up in the gas loop of the factory. Liquids produced would be worked away in the current tar work-up systems. Both products would thus contribute to the net product yield of the factories and a money value could be attached to it. Exploratory tests on a single gasifier, replacing up to 3% of the coal with waste, had no apparent effect on the operability/stability of the unit. Unfortunately the gasifier had only limited monitoring possibilities and a large scale test involving 13 gasifiers is planned. A number of important but as yet unknown effects are to be investigated and monitored in this test:

#### **3.1 Co-feeding of coal and waste**

The gasifiers are fed by lump coal using conveyor belts. For technical reasons, it is desirable to feed the waste with the coal. This poses a problem as a large percentage of this material is liquid to semi-liquid. It has been found that mixing such materials with absorbents/binders such as fly-ash, cement or clay results in a product with a dry, crumbly appearance. Laboratory work has shown that, upon pyrolysis, a coarse char is formed which should move with the coal through the gasifier. The possible long-term effect of this material on the integrity of the conveyor belts is currently being investigated. Furthermore it is important that no "sticky" material is deposited in e.g. the coal bunkers and coal-locks of the gasifiers.

#### **3.2 Effect on gasifier performance**

Once inside the gasifier it may be expected that, in the hot upper part of the gasifier (450 - 550°C), volatile material will be flashed off together with the tar of pyrolysis of the feed coal. The effect that the solid carbonaceous residue containing the inorganic binder may have on the operation of the gasifier will have to be considered. Part of the solids may break up and be swept out of the gasifier. The rest will move down with the coal through the various stages of fixed bed gasification and end up as part of the ash. It is known that an increase in ash content of the coal increases the oxygen and steam requirements per unit gas. As up to 50%

inorganic binder is used with the waste, the average ash content in the gasifier increases by 1 - 1½ %. Furthermore, it needs to be established whether the added inorganic binder breaks up further down in the gasifying vessel as this may lead to gas flow constrictions.

### **3.3 Down-stream effects - Primary tar separation**

Condensables, tar and gas liquor, are scrubbed down-stream from the gas phase. Coal used in the Sasol operation produces approximately 1½ - 2% of Fischer-tar. The addition of 3% of a 50/50 mixture of "foreign" organic matter and inert binder may as much as double the net hydrocarbon yield. It is not expected that capacity should be a problem in the current primary tar separator system. However separator performance will have to be carefully monitored. It is especially the possibility of emulsion formation which is of concern as this would severely reduce the efficiency of the separators.

### **3.4 Down-stream effects - Quantity and compatibility of products**

If the co-processed waste is of a coal tar origin, no problems, except for capacity down-stream, would be expected. However, if "non-coal" waste was to be present in the feed mixture, serious consideration should be given to the effect of interaction of species in the reactive vapour phase. The net product slate (including the raw gas composition) may change substantially which would affect down-stream processing as well as marketability of the final products. Homogeneity/miscibility of liquid materials will also have to be carefully investigated.

### **3.5 Down-stream effects - Gas liquor treatment**

Gas liquor is treated in a Phenosolvan unit. The possibility of a change in gas liquor quality cannot be overlooked as this may have detrimental effects on plant performance as well as on the quality of the products. Finely dispersed solid material finds its way via the gas liquor system to the Phenosolvan plant where filters are used to clear the feed. Performance of these filters will have to be monitored to ascertain whether additional fine solid material originating from the waste mixture, find its way down-stream.

### **3.6 Down-stream effects - Tar work-up plant**

Tar filtration is a critical pre-preparation step in the tar work-up plant. An increase in fine solid material in the tar feed, due to carry-over in the gasifier, may slow down filtration rate which in turn could limit the capacity of the work-up plant.

The possibility of a change in the composition of the tar feed (Par. 3.4) may also reduce existing plant capacity as well as product quality.

## **4. DEDICATED REACTOR**

A number of proprietary thermal processes have been developed with the purpose of recovering hydrocarbons from solid materials. These distillation/pyrolysis processes (pyrolysis units) are typically designed to remediate contaminated soils or for the recovery of oil from tar sands and

oil shales. An in-depth study into the suitability of such processes for application in the Sasol scenario has been made. Following in-house research up to process development unit (PDU) scale, it was concluded that the only feasible processes were those where direct heating is applied. These processes include inter-alia the Lurgi-Ruhrgas process, the AOSTRA-Taciuk process and the TOSCO process.

Pilot plant testwork has shown that up to 80% of the quinoline soluble material could be recovered as a liquid with a minor amount of gas make. The residual char was shown to exhibit a high-enough heating value to fuel the processes making them energy self-sufficient. Following primary Pilot plant work a number of important criteria had to be assessed:

#### **4.1 Co-processing with coal**

This not only has to be technically feasible but should make economic sense as well. Of the processes mentioned, use is often made of a solid heat carrier. Testwork has shown that properly graded coal could serve this purpose. Sasol's gasification coal produces a relatively small amount of Fischer-tar (Par. 3.3) which would contribute little to the net liquid yield during co-processing. However some small coal deposits, yielding up to 12% of Fischer-tar, are present in the Secunda (SFF) coal field. These coal types have been shown to be suitable for co-processing with some of the waste material increasing the net yield of liquids.

#### **4.2 Product compatibility with existing business**

A dedicated pyrolysis unit has the distinct advantage that it does not interfere with the core Sasol operations. Products are collected independently and can be marketed on their own. In the Sasol operation it could be economically advantageous to co-process the products of pyrolysis in the existing tar work-up facilities. However the aspects of plant capacity and more important, product compatibility as described in Par. 3.4 will have to be carefully considered. Although pyrolysis units operate on a continuous basis, feed preparation can be done batch-wise. This creates the opportunity of diverting incompatible feedstocks away from the existing tar work-up facilities. Such products could be sold as fuel oils. The option of co-processing with coal could be considered on such a "batch system" as well.

#### **5. SOIL REMEDIATION**

Many pyrolysis units have shown to be eminently suitable for remediating contaminated soils. This is a distinct advantage. Treating such soils in the Lurgi gasifiers is technically feasible if a low feed rate is maintained. This becomes impractical if the amount of soil needing thermal remediation is high.

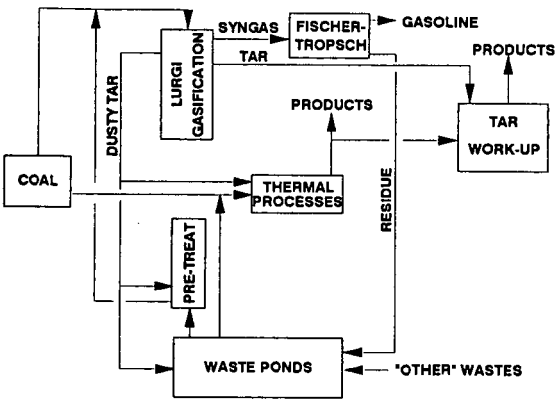
#### **6. CONCLUSION**

R&D work at Sasol has shown that thermal co-processing of coal and coal products will have a distinct role to play as part of a waste recovery project. Using the existing Lurgi gasifiers will result in a substantial saving in capital provided that due care is taken to preserve the integrity of current plant operation. The installation of a dedicated pyrolysis unit will be capital intensive. However, these costs could be off-set by, inter alia, avoiding the risk of production losses in current business. Pyrolysis units have the

added advantage that they are eminently suitable for the remediation of contaminated soils.

**ACKNOWLEDGEMENT**

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**FIGURE 1 THERMAL CO-PROCESSING  
OF COAL AND WASTE  
THE SASOL OPTIONS**

## CHARACTERIZATION OF COAL/WASTE COPROCESSING SAMPLES FROM HRI RUN POC-2

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**KEYWORDS:** coal liquefaction, coal/waste coprocessing, analysis

### ABSTRACT

Coal and waste materials (plastics and rubber) were co-liquefied during Run POC-2 in HRI's 3 T/D direct liquefaction process development unit under the DOE-sponsored Proof-of-Concept program. Analytical characterizations were conducted of well-defined samples from representative periods of the run to provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams. The characteristics of the products and process streams were dependent on both feedstock changes and operating conditions. Several unusual process oil characteristics were observed when wastes were coprocessed with coal, especially during the coal/plastic operation. Implications of these results for future coal/waste liquefaction development and analytical characterization of the materials are discussed.

### INTRODUCTION

Based on background work performed by the Consortium for Fossil Fuel Liquefaction Science<sup>1</sup> and the Pittsburgh Energy Technology Center, in July 1994 HRI completed nine days of coal/waste coprocessing during the DOE Proof-of-Concept direct liquefaction Run POC-2.<sup>2,4</sup> Several key accomplishments of the run were: subbituminous coal was processed without deposition problems such as were encountered at the Wilsonville pilot plant; an in-line hydrotreater was operated to produce high-quality distillate low in heteroatoms; an overall material balance of 99.6% was achieved; and the plant successfully converted fifteen tons of plastic and waste tires into premium fuels with high conversion and a lower hydrogen requirement than during coal-only operation. A diagram of the plant<sup>5</sup> as configured for HRI Run POC-2 is shown in Figure 1. CONSOL analyzed 65 samples collected throughout the run; sample points are shown in Figure 1. Run conditions for coal and coal/waste operating periods are compared in Table 1. The main variables were feedstocks, reactor temperatures, space velocity, recycle type (ashy or solids-free), and solvent/feed ratio. The periods were relatively constant in severity, according to HRI's index.

### ANALYTICAL APPROACH AND OBJECTIVES

Analysis of liquefaction process stream samples should always take place within a well-defined process framework. Sample origins and interrelationships should be understood in context to the process configuration and run conditions, and samples should cover representative periods of the entire run, not only the coprocessing periods. The analytical methods used here have been proven useful for liquefaction process stream characterization. Non-routine analyses were warranted in some cases for the coprocessing period samples. One objective was to determine the fates of the various waste feedstocks processed. Information is desired on the relative convertability of the feedstocks, the product streams to which the feedstocks are converted (bottoms vs. distillate), interactions of feedstocks, and their effects on product quality. In order to address these objectives, one must distinguish property characteristics reflecting feedstock differences from those caused by changes in other process conditions. In this case, process changes include: 1) ashy vs. ash-free recycle, 2) high make-up oil use in waste coprocessing periods, 3) high solvent/feed ratios in waste coprocessing periods, 4) ROSE-SR operations, and other factors, such as space velocity and catalyst age. Other performance issues of interest in HRI Run POC-2 include achievement of steady state unit performance (such as the ROSE deasher), retrograde reactions, and product stability issues.

### EXPERIMENTAL AND SAMPLE DESCRIPTION

Information about the samples analyzed and methods used is given in Table 2. Sample points, SP-xx, given in the table correspond to those shown in Figure 1. In the following discussion, the abbreviations shown in Table 2 will be used, e.g., NSB for naphtha stabilizer bottoms, DAO for deashed oil. Experimental details about most of the analytical methods used have been provided elsewhere.<sup>6,7</sup> GC/MS analyses were done with a DB-5 column, 30 m x 0.25 mm, 0.25  $\mu$ m film thickness. GC conditions were: 5 min at 10 °C; 2 °C/min to 100 °C, 4 °C/min to 320 °C, up to 20 min at 320 °C. The injection port was held at 300 °C. Carrier gas: He at 20 psig. One percent solution of make-up oil sample in tetrahydrofuran, or neat NSB samples were injected in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times.

### DISCUSSION

In this paper, we will highlight a few results that are of particular interest to coal/waste coprocessing. Most of the discussion will be concentrated on the



products (naphtha stabilizer bottoms (NSB) and ROSE-SR bottoms), the flashed second-stage oil (RLFVB), and ROSE-SR feed (VSB).

#### Plastics and Rubber Product Oils

Gas chromatography/mass spectrometry (GC/MS) total ion chromatograms are shown in Figure 2 for NSB product oils and the make-up oil. The make-up oil is used to supplement recycle when there is insufficient process-derived solvent. The NSBs contain paraffins with carbon numbers ranging up to about 24 (tetracosane, boiling point 736 °F); this generally is consistent with the expected boiling point of these products. The product from the coal/plastics and coal/rubber periods had more material boiling in the range 600-750 °F, in agreement with HRI's distillation data.<sup>4</sup> The make-up oil has a higher boiling point distribution than the NSBs, although the boiling points of the two overlap. The make-up oil may contribute to some of the higher boiling components seen in the NSBs from the coal/plastics and coal/rubber periods. Distillation, hydrogenation, and hydrocracking are all routes by which this higher-boiling make-up material may find its way into the NSB boiling range. Make-up oil comprised 27 wt % of the period 43 recycle stream composition and 43 wt % of the period 45 recycle stream composition, compared with none during the coal period 36. The contribution of make-up oil was exacerbated by the higher solvent/feed ratio of  $\approx 2.4$  in the waste/coal periods vs. 1.2 in the coal period. Thus, the higher-boiling material seen in the coprocessing period NSBs seems attributable to plant operating conditions, and not specifically to the feedstocks used. Since the plant was not in solvent balance during the coal/waste periods, sample and yield data may not represent plant operation at steady-state conditions.

#### Unusual Materials from Plastics Period

Significant amounts of ethylbenzene (EB) and methyl ethylbenzene (MEB) components were found in the NSB only from the plastics period, as determined by GC/MS (Figure 1, see marked peaks at retention times 16.77 and 21.85 minutes). Proton NMR confirms this, since distinctive peaks from ethylbenzene or diethylbenzene are present only in the spectrum (not shown) of the plastics period NSB product. These components are believed to be products from the liquefaction of the polystyrene. Thus, the presence of these components is attributable to the feedstock.

The DAO from the plastics period was extracted with THF and found to contain insolubles. This insoluble material is gray in color, waxy in appearance, and melts below 100 °C. Diffuse reflectance FTIR showed the material to contain methylene and methyl aliphatic groups, with essentially no aromatics or heteroatoms. Except for a more intense methyl C-H stretch peak in the DAO insolubles spectrum, it is very similar to that of a polyethylene film sample. The sharp doublets around 1470 and 720  $\text{cm}^{-1}$  are excellent matches with polyethylene. The peak at  $\approx 720 \text{ cm}^{-1}$  is indicative of long-chain paraffins. The elemental composition of the DAO insolubles is similar to that of the polyethylene feed, and they are almost identical in H/C ratio (not shown). Since this is apparently non-distillable wax, much heavier than previously observed,<sup>8</sup> we suspect that this material results from polyethylene liquefaction. In fact, the evidence strongly suggests that this material is unreacted or partially reacted polyethylene.

Variations in IOM across the vacuum still and ROSE unit were observed in CONSOL data. The coal conversion determined by CONSOL (Table 3) was 57.5% based the RLFVB sample, 96.8% based on the VSB sample, and 77.3% based on the ROSE bottoms sample (sequential points through the process). In addition to the increased IOM in the ROSE bottoms, a significant amount of the waxy IOM is recycled in the DAO. A relatively high preasphaltene concentration in the period 43 DAO coincides with the presence of IOM in this stream (Table 3). These results may reflect unusual solubility characteristics of liquefied plastics, especially polyethylene. The results suggest that for studying plastics liquefaction, one may need to develop a practical method to distinguish "dissolved" plastic (unchanged in molecular weight) from "converted" plastic (decreased in molecular weight).

The NSB from the plastic/coal period contained about 14 ppm (mg/kg) of sediment not present in other samples from this run, or in product oil samples from prior Wilsonville pilot plant runs or from HRI bench-scale runs. A portion of the sediment is slightly soluble in THF or pyridine. A sample of sediment was obtained for characterization by filtration of the NSB through a silver membrane filter, followed by a hexane wash and vacuum drying. The filter deposit was characterized in-situ by diffuse reflectance FTIR and SEM/EDX. FTIR indicated a primarily aliphatic material with a hydrogen-containing functional group (such as O-H); some aromatic and some carbonyl seem also to be present. SEM/EDX showed the deposit to consist primarily of sulfur, with smaller amounts of carbon and oxygen also evident. The collective evidence suggests that the bulk of the sample is elemental sulfur, which has little infrared activity and limited solubility in common solvents.

## CONCLUSIONS

Analyses were conducted on process oil samples from representative periods of HRI Run POC-2 in which coal, coal/plastic and coal/rubber were the feedstocks. Differences are apparent, some related to feedstock changes, others to operating condition changes. The high rate of make-up oil use in coal/plastics and coal/rubber periods may result in some of the higher boiling paraffinic components seen in NSBs from these periods. Significant amounts of ethylbenzene and methyl ethylbenzene components are present in the NSB product from coal/plastics operation; these appear to be products from the liquefaction of the polystyrene. There are unusual IOM characteristics in the coal/plastics period 43, perhaps as a result of unusual solubility characteristics of liquefied plastics, especially polyethylene. Heavy wax found as IOM in the DAO seems to be unreacted or partially reacted polyethylene. There is an apparent increase in conversion, followed by a decrease in conversion through a portion of the process. The conversion to THF solubles increased from 57% based on the second-stage product sample (RLFVB) to 97% based on the ROSE feed sample (VSB), and then decreased to 77% based on the ROSE bottoms sample. These results suggest a need to develop a method to distinguish "dissolved" plastic (unchanged in molecular weight) from "converted" plastic (decreased in molecular weight). The NSB sample from coal/plastics operation also contained a sediment not found in other samples.

Many products from liquefaction of plastics and rubber may not be chemically distinct from coal liquefaction products. It appears to be necessary to rely on "marker" compounds or materials (such as ethylbenzene from polystyrene) to demonstrate a non-coal origin of some product components. Proper interpretation of results is facilitated by analysis of liquefaction process stream samples within a well-defined process framework. Characteristics of products from HRI's Run POC-2 operation with coal/waste do not solely reflect feedstock differences from coal-only operation. Other conditions changed, as well, and the plant was not operating at steady-state when those materials were generated.

Run POC-2 operating experience should make it easier to avoid high make-up oil use in future runs with these feedstocks, since high make-up oil use lowers the quality of the analytical and yield information. There was no evidence that polystyrene did not convert completely, but there seem to be problems associated with polyethylene liquefaction (waxy DAO insolubles). The high oxygen content (32 %) of polyethylene terephthalate makes it less desirable as a feedstock, though it manifested no problems. It appears that polystyrene would be the preferred feedstock, based on this test. Liquefaction of the plastic feedstocks separately from each other would help resolve some issues. Coal/plastics product oil stability should be explored further.

## ACKNOWLEDGMENT

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TABLE 1. CONDITIONS FOR COMPARISON PERIODS OF COAL AND COAL/WASTE LIQUEFACTION

Process Condition	Period			
	21	36	43	45
Feed	100% Coal	100% Coal	30% Plastics, 70% Coal	25% Rubber, 75% Coal
Reactor Temp., °F				
K-1 (Ebullated-Bed)	775	810	810	810
K-2 (Ebullated-Bed)	830	835	830	830
K-3 (Fixed-Bed)	705	720	720	720
Severity, HRI Index	5.16	5.25	5.16	5.16
SV, lb MF coal/h/ft <sup>3</sup> reactor, per stage	30	40	30	30
Recycle/feed ratio	1.2	1.2	2.0	2.0
Recycle type	Ashy	Ashy	Solids-Free	Solids-Free
Other Information: run operated from June 1 through July 28, 1994; Black Thunder Mine subbituminous coal; ROSE-SR used for solids separation; 700°F* extinction recycle operation; catalyst addition rate in lb/T MF coal was 1.0-2.0 in K-1 and 2.0-2.5 in K-2; plastics were new in ratio 50/35/15 high-density polyethylene/polystyrene/polyethylene terephthalate; rubber was from scrap tires; Ni/Mo supported catalysts were Akzo AO-60 in K-1 and K-2 and Criterion 411 in K-3 (the on-line hydrotreater).				

TABLE 2. CONSOL ANALYSES OF SAMPLES FROM HRI WASTE/COAL COPROCESSING RUN POC-2

Sample Description (Name); Vessel; Sample Point	Periods	Technique & Information Sought (Refer to Key)
Atmospheric Still Bottoms (ASB); N-2 BTMS; SP-4	5, 15, 21, 36, 43, 45	A,B
Vacuum Still Bottoms (VSB); N-3 BTMS; SP-6	21, 36, 43, 45	E; THF Extract - A,B,F
Naphtha Stabilizer Bottoms (NSB); N-5 BTMS; SP-3	15, 21, 36, 43, 45	A,B,C,D
Recycle Oil; O-43 Oil; SP-11	5, 15, 34, 36, 43, 45	A,G,H; Dist. - A,B,G; Resid - E; Resid THF Extract - A,B,F
Reactor Liquid Flash Vessel Bottoms (RLFVB); O-46 Material; SP-9	5, 15, 21, 34, 36, 43, 45	A,G,H; Dist. - A,B,G; Resid - E; Resid THF Extract - A,B,F
ROSE Btms; O-63; SP-27A/B	15, 21, 34, 36, 43, 45	E; THF Extract -A,B,F
Deashed Oil (DAO); O-65 DAO; SP-25	15, 21, 34, 36, 43, 45	A,B,F; E(Some Periods); D
Make-Up Oil (M/U); Tank 4 Oil; SP-28	1	A,B,C,G

## KEY TO TECHNIQUES AND INFORMATION SOUGHT:

A = <sup>1</sup>H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors; B = FTIR in THF solution for phenolic -OH content; C = GC-MS for composition, carbon numbers of paraffins; D = special analyses as described in Discussion section (Period 43); E = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion; F = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition; G = microautoclave test with standard coal for donor solvent quality; H = 850°F distillation for distillate content.

TABLE 3. DATA INDICATING UNUSUAL IOM CHARACTERISTICS IN COAL/PLASTICS PERIOD

Period	Sample	Coal Conversion, wt % (a)	Phenolic -OH in Soluble Resid, mg/g	Component of Soluble Resid, wt %	
				Asph.	Preas.
15 Coal	Recycle Oil	87.3	0.18	7.3	6.5
	RLFVB	89.3	0.24	12.4	7.7
	VSB	—	0.20	13.1	3.2
	ROSE Btms	86.1	0.29	28.8	14.7
	DAO	—	0.14	5.5	0.7
21 Coal	RLFVB	92.5	0.27	18.4	6.1
	VSB	91.9	0.22	18.6	2.8
	ROSE Btms	91.8	0.28	18.8	8.3
	DAO	—	0.14	7.0	1.4
36 Coal	Recycle Oil	91.3 (91.0*)	0.35 (0.30*)	13.4 (12.2*)	7.7 (5.4*)
	RLFVB	—	0.45	21.8 (20.0*)	3.7 (3.9*)
	VSB	91.2	0.36	20.7	2.7
	ROSE Btms	91.9 (90.1*)	0.55 (0.44*)	25.9 (23.5*)	8.5 (12.7*)
	DAO	—	0.24 (0.29*)	5.8 (8.6*)	0.1 (0.3*)
43 Coal/Plastics	Recycle Oil	—	0.12	21.0	2.6
	RLFVB	57.5	0.28	19.8	9.8
	VSB	96.8	0.16	13.2	1.0
	ROSE Btms	77.3	0.23	22.0	6.7
	DAO	—	0.13	5.0	11.1

\* From Per. 34, at same conditions, but without Mo additive used in Per. 36.  
(a) MAF % Conversion =  $[(100 - \text{ash\% in dry feed}) - (\text{sample \% IOM}) * (\text{ash\% in dry feed}) / (\text{sample \% ash})] * 100 / (100 - \text{ash\% in dry feed})$ ; plastics ash content was assumed to be 0%.

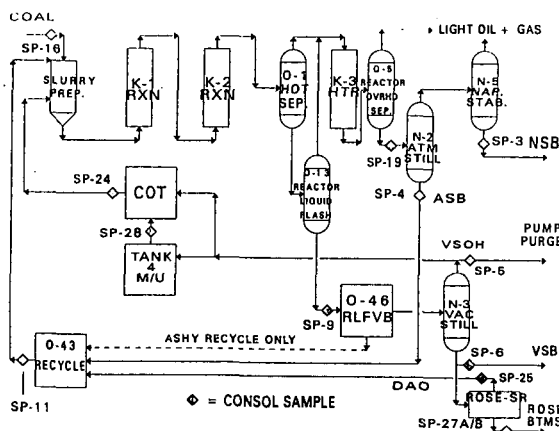


Figure 1. Diagram of the HRI Proof-of-Concept Plant Showing Sample Points, as Configured for Run POC-2.

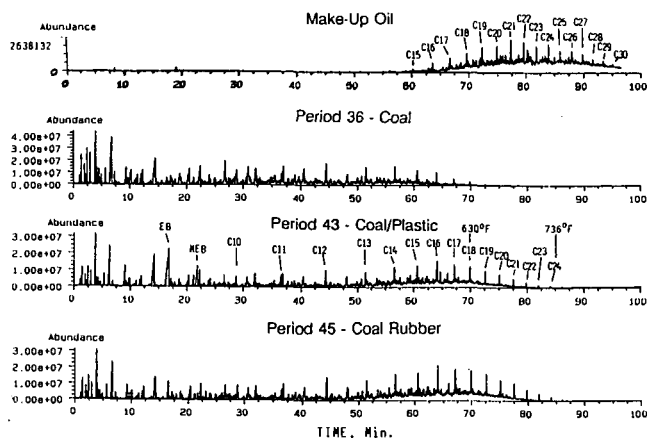


Figure 2. GC-MS Total Ion Chromatograms of Make-Up Oil and Product Oils From HRI Run POC-2.